(Medical and Chemical Series, No. 10.)
(Dyes and Tans.)

THE
AGRICULTURAL LEDGER.

1897—No. 6.

MYRICA NAGI.
(KAIPHAL BARK.)

[*DICTIONARY OF ECONOMIC PRODUCTS, Vol. V., M. 869-77.*]

THE TINCTORIAL PROPERTIES OF KAIPHAL BARK AND AN ANALYSIS OF THE COLOURING PRINCIPLE.

By PROFESSOR JOHN JAMES HUMMEL *and* MR. ARTHUR GEORGE PERKIN. *With an Introduction by* MR. DAVID HOOPER.

Other PAPER that may be consulted:
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(3) To admit of the circulation, in convenient form, of information on any subject connected with agriculture or economic products to officials or other persons interested therein;

(4) To secure a connection between all papers of interest published on subjects relating to economic products and the official Dictionary of Economic Products. With this object the information published in the ledgers will uniformly be given under the name and number of the Dictionary article which they more especially amplify. When the subject dealt with has not been taken up in the Dictionary, the position it very possibly would occupy in future issues of that work will be assigned to it.

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INTRODUCTION.

India is naturally rich in dyeing agents, and those of acknowledged value have been in use for so many years that it would seem superfluous to suggest changes in the industry. The introduction of aniline dyes, on account of their cheapness and ease of application, have to some extent reduced the trade in raw and bulky colouring materials; but there are still many tints obtained by the dyer in this country which cannot be imitated by artificial means. The indigenous vegetable colours are derived from plants, which, if not wild, are easily cultivated, and the Native operator in outlying districts is quite satisfied with his crude methods of dyeing passed down through many generations.

The attention that has recently been paid by experts to the different coloured dye-stuffs of India has resulted, for the first time, in an attempt to classify these articles scientifically. Mr. (now Sir Thomas) Wardle, of Leek, and Professor Hummel, of Leeds, have experimented with the dyes with regard to their technical properties, while Dr. Schunck and Mr. A. G. Perkin have elucidated the subject by their analyses of the actual colouring principles found in the raw products. As far as the yellow dye-stuffs have been investigated by

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Messrs. Hummel and Perkin conjointly, there are those applied with the aid of mordants having a similar chemical composition, while others which are applied direct are related in their tinctorial power to the constitution of their active principles. The experiments have enabled the authors to pass an opinion on the value of the dye-stuffs in European commerce and to indicate the permanent or fugitive nature of the colours obtained from them.

One of the most interesting results of the enquiry has been the discovery of a bark possessing a rich yellow colouring matter, far superior to many well-known dye-stuffs. The bark in question is derived from **Myrica Nagi** and has hitherto been collected and used for its medicinal properties which are described in Sanskrit works of great antiquity. The drug is astringent in its properties and has been used for tanning. The only reference to its use as a dye is very vague, and its properties are not known among Native traders. In the following paragraphs we have placed together all the available information on this article concluding with the exhaustive analysis recently made of the bark in England.

Myrica Nagi is an evergreen, diœcious tree belonging to the MYRICACEÆ, a small natural order of plants placed between the URTICACEÆ and the CASUARINEÆ. It is met with in the sub-tropical Himálaya from the Ravi eastward, also in the Khasia Mountains, Sylhet and southwards to Singapore, and is distributed in the Malay Islands, China and Japan.

Some confusion has arisen from the fact that the tree has been variously named by botanists, but from a thorough examination of the genus by Sir J. D. Hooker, it has been decided that the following six names refer to one and the same species—the tree under consideration :—

Myrica esculenta, *Buch.-Ham.*
M. Farquhariana, *Wall.*
M. integrifolia, *Roxb.*
M. missionis, *Wall.*
M. rubra, *Sieb. et Zucc.*
M. sapida, *Wall.*

The English name of the tree is Box Myrtle. In China it is called *Yangmœ* and in Japan *Shibuki*. *Kaiphal* is the name applied in India both to the tree itself and to the bark or portion of the tree used by the Natives.

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The bark is collected in the Himálaya at altitudes of from 3,000 to 6,000 feet, and is occasionally exported in large quantities to the plains in the North-Western Provinces and other parts of India, in recent years to the extent of 50 tons per annum. In Bombay it is worth from 1 to 2 rupees per maund of 41℔.

The bark is used as a tan for fancy leather work, and according to **Mr. W. Coldstream** it is used in Sirmur in the Simla District for dyeing a peculiar pink. It is also employed in medicine and is kept in stock in most of the Native drug shops in Northern India. In Sanskrit works the bark is described as heating, stimulant, and useful in diseases supposed to be caused by deranged phlegm, such as catarrhal fever, cough and affections of the throat. Like most Eastern remedies the bark is usually prescribed in the form of a mixture with other stimulants, alteratives and aromatics. **Dr. U. C. Dutt** speaks of the powdered bark being simply used as a snuff for catarrh with headache. *Kaiphal* mixed with ginger, according to some doctors, is the best medicine for cholera. Hindus and Mahomedans use *kaiphal* in the present day as an astringent, carminative and tonic, and prescribe it for chronic cough, fever and piles. Mixed with vineger it strengthens the gums and cures toothache. It will be seen that it is used where astringents are required, and the dose is stated to be sixty grains of the powdered bark.

The astringent properties of this bark are not utilised in India only as they are recognised in Japan and America. In an article on a number of tanning materials used in Japan, **Mr. J. Ishikawa** (*Chemical News*, December 3, 1880, p. 275) gives the result of his analysis of *shibuki* bark, obtained from **Myrica rubra,** and shows that the specimens submitted to him contained from 11 to 14 per cent. of tannin.

An American species of **Myrica (M. asplenifolia,** *L.*) was examined in 1894 by **Mr. C. C. Manger,** who found the following maximum proportions of tannin in the moist state:—leaves, 9·42; stem, 3·72; rhizome, 5·47. In an absolutely dry state the proportions were as follows:—leaves, 10·28; stem, 4·16; rhizome, 6·00.

The bark of **Myrica Nagi,** when collected in India from large trees, is about half an inch thick, extremely scabrous, pitted from the separation of pieces of suber, of a mottled rusty brown and dirty-white colour, suber warty; substance of bark and inner surface

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of a dull red colour; it yields a red colour to water; taste strongly astringent. Examined miscroscopically, within the suberous layer is seen a remarkable stratum of stony cells; the parenchyma throughout is loaded with red colouring matter, and permeated with large laticiferous vessels, from which a gummy latex exudes when the bark is soaked in water. In a powdered condition it acts as an irritant on the mucous membrane of the nostrils.

A sample of *Kaiphal* from Bombay, consisting of thick pieces of bark, evidently taken from old trees, contained 11 per cent. of moisture and yielded 7 per cent. of ash. Estimated for tannin, it afforded 13·7 per cent. The lead compound of the tannic acid left when ignited 30·72 per cent. of oxide, a result which compared very closely with the amount found in the compound separated from the "kino," namely, 31·88 and 30·36 per cent. in two estimations. The tannic acid, separated from the tincture by evaporation and treatment with water, gives a bluish-purple colour with ferric chloride, but on adding this reagent to a decoction of the bark, a dirty green precipitate is formed.

Mr. H. R. Procter, Lecturer on Leather Industries, Yorkshire College, Leeds, gives the following average of four separate analyses of the bark of Myrica Nagi:—

Tannin matters absorbed by hide	27·3
Soluble non-tanning substances	7·9
Fibre, and insoluble matters	52·3
Moisture	12·5
	100·0

It will be observed that the variability in the amount of the tannin in these barks has a wide range. The sample examined in Leeds by Mr. Procter contained about double the amount of tannin to that purchased in the Bombay market. Like most of the astringent barks the richness of the active principle may be attributed to the age of the tree or portion of the tree, branch or stem, which afforded the sample.

In 1889, Dr. Dymock sent the writer for analysis a sample of Myrica Kino. This substance occurred in a granular condition; it was of a dark purplish-red colour, hard and brittle when dry, and without any peculiar odour. It dissolved almost completely in boiling water, but a flocculent red precipitate separated when the decoction cooled.

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A tincture made with rectified spirit was of a fine, bright red colour and very acid in reaction. The tannic acid gave a greenish colour with ferric chloride, and was estimated in a cold watery infusion of the drug with a solution of plumbic acetate. The "Kino" had the following composition:—

Pure tannic acid	60·8
Insoluble in water	3·3
Moisture	9·8
Ash	10·8
Sugar, etc.	15·3
	100·0

The large amount of carbonated ash left, on incineration, points to the probability of some of the tannic acid existing in combination with a mineral base, and this was really so. A large quantity of a substance readily reducing Fehling's test, is not a usual constituent of a natural astringent secretion like Kino, and it was interesting to find that the above substance had been prepared by evaporating a watery decoction of the bark; this would account for the presence of mineral matter and glucose in the extract.

For several years past Professor Hummel, of Leeds, has been working on the Dyes and Tans of India, and recently, in conjunction with Mr. A. G. Perkin, who has submitted each dye to a critical chemical analysis, a most valuable series of papers has been published on Indian dyeing materials.

In a letter dated the 22nd November 1894, Sir F. A. Abel, Bart., K.C.B., Secretary and Director of the Imperial Institute, communicated to Dr. Watt some of the results of these investigations, and referring to the labours of Professor Hummel he wrote: "He also informs me that he has completed preliminary dyeing experiments with the whole of the Indian dye-stuffs in the Museum of the Yorkshire College, and he sends me a list of eight which are sufficiently rich in colouring matter to render them worthy of examination both chemically and tinctorially in preference to others. He asks whether I can obtain for him within, say, a year from this time from 1 to 2 cwt. of three or four of these materials which he names in the order of their merit of dye-stuffs."

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In the list which Sir F. Abel appended to his letter and which specifies the dyes arranged in the order of their tinctorial value, it is seen that the bark of **Myrica Nagi** takes the highest place.

1. **Myrica Nagi** (bark).
2. **Delphinium Zalil** (flowers).
3. **Carpesium abrotanoides** (whole plant).
4. **Nyctanthes Arbor-tristis** (flower tubes).
5. **Kandelia Rheedii** (wood).
6. **Gossypium herbaceum** (flowers).
7. **Thespesia populnea** (flowers).
8. **Mangifera indica** (bark).

The Reporter on Economic Products to the Government of India having supplied the required quantity of Kaiphal bark next year Messrs. Hummel and Perkin published the results of their work in this direction as far as they had gone. The paper was read before the Society of Chemical Industry, London, and printed in the Journal for May 31, 1895. It was sent as a contribution from the Clothworkers' Research Laboratory in the Dyeing Department of the Yorkshire College, Leeds, and was entitled "The Tinctorial Properties of some Indian Dye-stuffs, Part II." The following extract gives the conclusions the authors arrive at with regard to **Myrica** :—

"The dyeing properties of **Myrica** bark, although generally similar to those of other yellow mordant dye-stuffs, differ in some respects from any one of them. On wool, with chromium mordant, it gives a deep olive-yellow, and with aluminium a dull yellow, similar to the corresponding colours obtained from quercitron bark, but much fuller; with tin mordant, however, it gives a bright red-orange, redder in hue than that given by quercitron bark, and fuller even than that given by an equal percentage of Persian berries, to which otherwise it is very similar; with iron mordant it gives a dark greenish-olive like that obtained from quercitron bark, but again fuller; it seems indeed to have a greater colouring power than all other natural yellow mordant dye-stuffs.

"On cotton with aluminium and iron mordants it dyes colours which are more similar to those obtained from old fustic than from quercitron bark, the colours with iron mordant, for example, not exhibiting the dark and bluish hue given by the latter, as though tannin matter were absent.

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" Compared with old fustic, on wool mordanted with aluminium, 3·7 grms. **Myrica** bark equal in dyeing power 5 grms. old fustic but it gives a much duller olive-yellow colour. Compared with Chromium mordant on wool, 2 grms. **Myrica** bark are equal to 5 grms. old fustic, but here, too, the colour is much redder or browner.

" The comparative richness in colouring power of **Myrica** bark, and the full, brilliant red-orange given with tin mordants on wool, are sufficiently interesting to warrant us in examining this bark thoroughly, more particularly since it is evident that its utility as a dye-stuff is unknown to the Hindus."

Sir F. A. Abel, when forwarding copies of the above paper from the Imperial Institute, on the 27th June 1895, made a request for a larger supply of the bark to allow of a complete set of experiments being carried out, and in accordance with the request about 70℔ of Kaiphal were collected by the Reporter on Economic Products in Simla and despatched to London in November.

In the course of a few months the following important paper on a full analysis of Kaiphal appeared in *The Transactions of the Chemical Society.* The paper is printed *in extenso,* with the exception of the experimental data and calculations of the formulæ:—

Contribution from the Clothworkers' Research Laboratory, Dyeing Department, Yorkshire College. The colouring principle contained in the bark of **Myrica Nagi**. *Part I.*

By ARTHUR GEORGE PERKIN and JOHN JAMES HUMMEL.

In the course of examining the tinctorial properties of some Indian dye-stuffs (*J. Soc. Chem. Ind., 1895*) our attention was especially attracted by the behaviour of the bark of **Myrica Nagi.** Not only did the colouring power compare favourably with that of such well-known dye-stuffs as old fustic and quercitron bark, but in some respects it seemed to differ from all other yellow mordant dye-stuffs. Having subsequently received a larger supply through the kindness of the authorities of the Imperial Institute, London, the chemical examination of this dye-stuff was undertaken, and the results are recorded below.

EXPERIMENTAL PART.

The ground bark (1,000 grams) was digested for six hours with ten times its weight of boiling water, the mixture strained through

calio, and the residue treated again in a similar manner. Experiment showed that by extracting the filtrate with ether a small amount of colouring matter could be thus obtained; the ethereal extract separated, however, with difficulty from the aqueous liquid, and as also a very large quantity of ether was necessary for this process, the following method appeared preferable. To the combined boiling aqueous extracts, a solution of 60 grams of lead acetate was added, when a bulky, yellowish precipitate was obtained, which, on prolonged boiling, became dirty white; this consisted almost entirely of the lead compound of tannin matter, and contained but a trace of colouring matter. This was removed by filtration, washed with water, and the filtrate treated with more lead acetate solution until a precipitate was no longer formed; the lemon-yellow lead compound was then collected, washed, and decomposed, while still moist, by means of boiling dilute sulphuric acid. The brown liquid, which now contained the colouring matter, was removed from the lead sulphate by decantation, and extracted twice with ether; the yellow crystalline residue left on evaporating the ethereal extract was dissolved in a little alcohol, and the solution diluted with boiling water. The crystals which separated on cooling, were collected and extracted two or three times with small quantities of boiling acetic acid in order to remove a colourless wax-like substance which was present in some quantity. By recrystallisation from dilute alcohol, the product was obtained in a pure condition. The yield of colouring matter from 100 grams of bark averaged from 0·23 to 0·27 gram.

The ultimate analysis indicated the formula $C_{15}H_{10}O_8$, which requires $C = 56{\cdot}60$; $H = 3{\cdot}14$ per cent.

It formed a mass of light yellow, glistening needles closely resembling quercetin in appearance, and melting above 300° with decomposition. When heated between watch glasses, the mass became carbonised, and a small quantity of yellow vapour was evolved, which, on cooling, condensed to minute needles of the unchanged substance. It is very sparingly soluble in boiling water, somewhat readily in alcohol, and almost insoluble in chloroform and acetic acid. Though closely resembling in appearance the colouring matters of the quercetin group, it is readily distinguished from those at present known by the colour changes it produces when dissolved in alkaline solutions. With dilute potassium hydroxide, a green solution is first

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formed; this, on exposure to air, rapidly assumes a deep blue tint, which in its turn gradually becomes dull red-violet. With strong alkali a fairly permanent orange-coloured liquid is obtained which, when diluted, passes through the colour changes recorded above. A solution of ammonia produced somewhat similar results, the colour obtained having, however, a redder tint. The addition of lead acetate to its alcoholic solution throws down a reddish-orange precipitate which becomes yellower on boiling. The colouring matter dissolves in cold sulphuric acid, forming a deep red solution, which deposits the unchanged substance on adding water. Its alcoholic solution is coloured brownish-black by ferric chloride. In examining the dyeing properties of this new colouring matter, for which we propose the name *myricetin*, experiments were carried out with it side by side with equal weights of pure preparations of quercetin, fisetin, morin, gentisin, and euxanthone, using woollen cloth mordanted with chromium, aluminium, and tin. It was at once apparent that a strong resemblance existed between the shades given by myricetin, quercetin, and fisetin, in fact, so similar were they, that unless placed side by side one might easily be mistaken for the other. These differences are best seen in the table.

This table shows that, so far as its dyeing properties are concerned, morin belongs to a distinct group, and the same may be said regarding gentisin and euxanthone.

By examination in Zlesel's apparatus, myricetin was found to contain no methoxyl-groups.

		Chromium.	Aluminium.	Tin.
1	Myricetin	Red-brown	Brown-orange	Bright red-orange.
	Fisetin	,,	Brown-orange, inclining to red.	Slightly less red.
	Quercetin	,,	Brown-orange, inclining to yellow.	Bright orange.
2	Morin	Olive-yellow	Dull yellow	Bright yellow.
3	Gentisin	Green yellow, dull and pale.	Bright yellow tint, very pale, scarcely dyed.	Cream colour, scarcely dyed.
	,,			
	Euxanthone	Dull brown, yellow.	Bright yellow, pale.	Bright yellow, tint very pale, scarcely dyed.

Myricetin Sulphate, $C_{15}H_{10}O_8,H_2SO_4$.—In order to determine the molecular weight of myricetin, its behaviour towards mineral

and hydrochloric acid the phloroglucinol reaction, and, further, that when heated to 240° the residue had the properties of pyrogallol, and not of phloroglucinol. It was therefore *gallic acid*.

The filtrate from the lead precipitate was treated with sulphuric acid to decompose lead compounds, the lead sulphate removed by filtration, the filtrate extracted with ether, and the extract evaporated. The residue thus obtained was too small for complete purification, but it gave the phloroglucinol reaction, and without doubt consisted chiefly of this substance.

The principal products of the action of fused alkali on myricetin are therefore *gallic acid* and phloroglucinol.

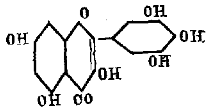
Action of Bromine on Myricetin.—To a thin paste of myricetin in acetic acid, the amount of bromine necessary for the formation of a tetrabromo-compound was added. Hydrogen bromide was evolved, and a clear solution gradually formed; this, after standing over night, was poured into about six times its bulk of water. At first crystals were slowly deposited, but after some time a small quantity of flocculent matter also separated. The product was collected and purified by several crystallisations from dilute acetic acid. As the yield obtained in this way was somewhat unsatisfactory, experiments were carried out on the bromination of myricetin suspended in carbon bisulphide at 100°. By these means the quantity of product obtained was found to be considerably increased.

It was obtained in the form of brownish-orange, prismatic needles, melting and decomposing at 235—240°, readily soluble in acetic acid, slightly less so in alcohol. Alkaline solutions dissolve it at first with a yellow colouration, which on exposure to air becomes red, and finally passes into dirty brown. Its alcoholic solution gives with ferric chloride a deep blue colouration. With mordanted calico, it dyes shades considerably yellower than those of myricetin itself, and more resembling those yielded by gallacetophenone.

Although the analytical numbers agree closely with those required by tetrabromomyricetin $C_{15}H_6O_8Br_4$, and moreover the production of such a compound is in harmony with the probable constitution of this substance, yet on account of the peculiarity of its properties considered side by side with those of the bromine derivatives of quercetin, morin, and luteolin, some little doubt must be entertained

as to its identity until a molecular weight determination can be carried out. By the introduction of bromine into the above colouring matters, their reactions with ferric chloride are but little altered; moreover, these compounds are considerably less soluble than the colouring matters themselves.

In examining the results of this investigation, but little doubt can be entertained that myricetin is a member of the quercetin series. Its formula, its reactions with mineral acids, and the number of hydroxyl groups it contains, when considered with the results of its decomposition with alkali, are all in harmony with this suggestion. Moreover, its dyeing properties are very similar to those of quercetin and fisetin. Before absolutely deciding its constitution, it will be necessary to examine its methyl and ethyl ethers and their decomposition products; unfortunately, the difficulty of isolating sufficient substance for this purpose may delay this investigation for some time. There appears, however, every probability that myricetin, $C_{15}H_{10}O_8$, will thus be shown to have the constitution of an hydroxy quercetin,—



Its colour reactions in alkaline solution are evidently due to the oxidation of the pyrogallol nucleus it contains.

Dyeing Properties.—The tinctorial power of the product now examined was much less than that of the small sample of bark with which the earlier experiments were made, and which had a much smoother exterior, and was labelled **Myrica rubra**; moreover, it gave somewhat different shades with the different mordants. On striped mordanted calico, the present sample gave with alumina a comparatively dull yellow, inclining to pink on a weak mordant, and with iron a purplish-grey, as if tannic acid were present. Its colouring power was much less than that of old fustic and quercitron bark. On the other hand, our former sample gave with alumina a

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full yellow, distinctly stronger, although somewhat duller, than those given by the dyewoods just mentioned, and the colour with iron mordant gave little or no indications of the presence of tannic acid. On wool mordanted with chromium, aluminium, and tin, and dyed with 40 per cent. of our latest sample, greenish-olive, olive-yellow, and yellow colours respectively were obtained, all very pale and dull, whereas with the same mordants our former sample yielded deep olive-yellow, dull-yellow, and bright red-orange, the two first reminding one of the corresponding colours obtained from quercitron bark, the latter being very similar to those given by Persian berries.

These results show either that the colouring properties of **Myrica Nagi** are somewhat variable, according to the age of the tree or branch from which the bark is taken, or that there may be different species of **Myrica**, each with slightly different tinctorial properties. The comparative richness of some of the barks, however, warrants us in directing the attention of native dyers of India to its probable utility as a yellow dye-stuff.

G. I. C. P. O.—No. 107 R. & A.—14-7-97.—2,200—W. B. G.

All communications regarding THE AGRICULTURAL LEDGER should be addressed to the Editor, Dr. George Watt, Reporter on Economic Products to the Government of India, Calcutta.

The objects of this publication (as already stated) are to gradually develop and perfect our knowledge of Indian Agricultural and Economic questions. Contributions or corrections and additions will therefore be most welcome.

In order to preserve a necessary relation to the various Departments of Government, contributions will be classified and numbered under certain series. Thus, for example, papers on Veterinary subjects will be registered under the Veterinary Series; those on Forestry in the Forest Series. Papers of more direct Agricultural or Industrial interest will be grouped according as the products dealt with belong to the Vegetable or Animal Kingdom. In a like manner, contributions on Mineral and Metallic subjects will be registered under the Mineral Series.

This sheet and the title-page may be removed when the subject matter is filed in its proper place, according to the letter and number shown at the bottom of each page.